# GRAVITY-DRIVEN AND SURFACE TENSION-DRIVEN CONVECTION IN SINGLE CRYSTAL GROWTH

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## ABSTRACT

Analytical and mathematical studies of the floating-zone and the Czochralski techniques of growing single crystals are being conducted. The objective of these studies is to elucidate the role of convection in single crystal growth. Gravity-driven and surface tension-driven convection and possible couplings between these two convective modes will eventually be incorporated into the analyses. The analyses are expected to provide a basis for predicting the effects of a zero-gravity environment on crystal growth.

## INTRODUCTION

The possibility has been suggested that single crystals of unprecedented perfection can be grown in a zero-g environment. One of the main advantages of a zero-g environment foreseen for achieving such a result is that gravity-driven convection is eliminated (Ref. 1). Gravity, however, is not the only driving force for the transfer of mass. Liquid-vapor surface tension (and, possibly, solid-liquid interfacial tensions) also is a potential driving force for fluid motion. A definite conclusion regarding the benefits of eliminating gravity-driven convection, therefore, requires that two questions be considered further:

- In what manner does convection affect crystal growth and thereby influence crystal perfection?
- What extent of convection is likely to be encountered under various g conditions?

Before these questions are explored further, the crystal-growing techniques to which the present study is limited should be defined; i.e., the floating-zone and the Czochralski technique. The floating-zone technique or some variant of it is foreseen as being the technique most directly adaptable to zero-g environment and was therefore chosen for study. The Czochralski technique is also being studied because high quality semiconductors are now routinely produced by this technique. Crystals produced by the technique are thus readily available to check theoretical predictions and to provide standards with which crystals produced by other techniques can be compared. Also, in common with the floating-zone technique, the Czochralski technique involves no mechanical restraint on the periphery of the growing crystal. Some features of crystals produced by either of these two methods, therefore, will be comparable.

The salient features of the floating-zone technique are illustrated in Fig. 1. A molten band or zone is produced in a rod of polycrystalline material. The method of heating may be radiant, induction, or electron-beam bombardment, depending upon the physical characteristics of the particular material being processed. The molten zone is caused to pass along the rod, by moving the heat source, with melting occurring at one interface and freezing at the other. By introducing a properly oriented seed at the freezing interface and controlling the rate of zone travel, single crystal growth can be accomplished. The main advantage of the technique is that crucible-melt contact is avoided thereby eliminating a potential source of contamination. Under 1-g condition, however, the size of the molten zone is limited by the need for surface tension to balance the hydrostatic pressure of the liquid. Also, a limiting factor is the tendency of surface tension to reduce the liquid surface area. A long thin molten zone would show a tendency to separate.

The essential features of the Czochralski technique are shown in Fig. 2. Material melt is contained in a heated crucible. A seed crystal is brought into contact with the melt surface. After wetting is completed, the seed is slowly withdrawn. The diameter of the pulled crystal is controlled by controlling the temperature of the melt and the rate of crystal pulling. Also, the crystal is rotated as it is withdrawn to eliminate thermal asymmetry. The melt may also be rotated for greater control of the thermal conditions.

## CONVECTION AND CRYSTAL PERFECTION

Consider again the question of the relationship between convection and crystalline perfection. Convection may affect crystal growth processes indirectly by altering the temperature and concentration field throughout the fluid phase. Because both convection and solidification mechanisms, however, depend directly on local temperature and concentration conditions, convection and solidification are seen to be dependent processes. In fact, they may be said to be coupled processes. Each is a response

to imposed variations of a variety of possible independent parameters among which gravity must be numbered. The degree and manner of occurrence of either or both processes is thus interrelated. For example, the occurrence of compositional cells which have their origin in constitutional supercooling depends on the temperature gradient in the liquid phase (Ref. 2). The steeper the gradient, the less likely the occurrence of compositional cells. The steeper the external temperature gradient, however, the more likely that convection will result. The internal temperature gradient near the solid-liquid interface therefore may be reduced. The presence of a moving solid-liquid interface which is liberating heat, in turn influences the convective field.

Incidentally, the appearance of the various interface morphologies as a function of the liquid temperature gradient near the solid-liquid interface is shown in Fig. 3. The morphology changes from a planar to a cellular configuration as the temperature gradient decreases and the degree of constitutional supercooling increases (Ref. 3). The appearance of the cells attributed to constitutional supercooling is quite similar to the appearance of convection cells produced in thin layers of liquids. This is discussed later.

Another consideration in connection with the influence of convection on crystal perfection is the scale of fluid motion. This may be classified as macroscopic or microscopic. Both can affect crystal growth processes. To illustrate how macroscopic flows exert an influence on subsequent crystal perfection: the solid-liquid interface shape of a growing crystal is an important parameter of dislocation densities. This is because of the relationship between the shape of the interface to the thermal conditions of growth and the associated thermal stresses.

Figure 4 shows the temperature isotherms associated with a concave (to the liquid) interface shape. Near the solid-liquid interface, the temperature at the outer surface of the solid is lower than the temperature near the center. Thermal contraction, therefore, causes the outer surface to exert a compressive stress on the core of the crystal while the surface itself is in a state of tension (Ref. 4). If the solid-liquid interface is convex to the melt, the inner core will be in tension and the outer in compression. When the stress $\sigma$ exceeds the yield stress $\sigma_y$, plastic flow will occur which will relieve itself into dislocations. Convection can be expected to exert a significant effect on the macroscopic interface shape profiles. Figure 5 indicates the result of convection on the macroscopic interface shape during a horizontal zone melting of an organic compound.

On a microscopic scale, convection is probably the cause of many puzzling crystalline imperfections. For example, temperature fluctuations having their origin in turbulent convection can result in fluctuations of crystal growth rate. Because the concentration of solute incorporated

into a solid is a function of the growth rate, the result of growth rate fluctuations is banding of solute in the solid (Ref. 6). Local segregation of solute on a microscopic scale can also lead to the introduction of dislocation lines at the bounding surfaces of the segregate (Ref. 7).

Although convection is recognized as being a possible cause of microscopic crystalline imperfections, the type or mode and scale of convection leading to these imperfections is just beginning to be investigated. The preceding discussion is a brief general indication of how convection can affect the perfection of single crystal growth from melt. Some possible modes and the extent of convection under varying gravity fields are now discussed.

## GRAVITY AND SURFACE TENSION-DRIVEN CONVECTION

As indicated in the opening paragraphs, gravity is not the only possible motive force for fluid motion. Surface tension (and possibly solid-liquid interfacial tension) and the volume change which occurs on crystallization are also possibilities. In the present study the latter type of convection is not being considered. For the case of crystal growth by the floating-zone technique in which large temperature and concentration gradients at a free liquid surface are certainly present, considerable convection, which has surface tension as its driving force, can be expected. Fluid flow caused by surface tension gradients is called the Marangoni effect. (Several excellent general reviews of surface tension flows are given in Ref. 8.) If a free liquid surface experiences a temperature or concentration gradient, a surface tension gradient will result because surface tension is a function of temperature and concentration. Along the surface the liquid will flow from the region of low surface tension to one of high surface tension. Usually this will be from hot regions to colder regions because surface tension generally decreases with increase of temperature. The liquid moves the fastest near the surface, the depth of the disturbance depending on a variety of hydrodynamic parameters.

The occurrence of "tear drops" in a wine glass is a common illustration of the Marangoni effect. In this case evaporation of alcohol leaves the layer of liquid on the wetted glass wall with a higher surface tension than in the bulk of the liquid. As a result, liquid on the glass walls continuously draws up more liquid from the bulk until a "tear" is formed. When the "tear" becomes large enough it falls back into the liquid. Another less commonly observed fluid motion which may be classified as microscopic convection also has its origin in surface tension gradient. A cellular motion results if a thin layer of fluid is heated from below and cooled from above. This type of convection flow was first investigated by Bénard in 1900.

Lord Rayleigh developed a theory for cellular convection on the basis of an unstable density gradient. Rayleigh's theory, however, did not

agree with all experimental observation. For example, cellular convection was found in shallow pools cooled from below; a stable situation according to Rayleigh's theory. Also the flow patterns observed in some instances were opposite to those predicted by Rayleigh's theory. Hot liquid was observed rising below centers of depression, whereas hot liquid would be expected to coincide with elevated regions if the flow were gravity driven (see Fig. 6). The discrepancies were resolved when both gravity and surface tension were recognized as possible motive forces for fluid flow. Couplings between surface tension and buoyancy were also recognized as a possibility.

In one analysis of cellular convection (Ref. 9) a stability criterion for surface tension-driven flows based on a dimensionless number B is given. This number known as the Marangoni number expresses the ratio of surface tension to viscous forces and is defined as

$$B = \frac{-\frac{d\sigma}{dT}\frac{dT}{dy}d^2}{\rho \nu \alpha}$$

where $dT/dy$, $\nu$, $\alpha$, $\rho$, and $d$ are vertical temperature gradient, kinematic viscosity, thermal diffusivity, density and thickness of the fluid layer, respectively. The term $d\sigma/dT$ represents the rate of change of surface tension with temperature.

For gravity-driven cellular convection the stability criterion is based on the Rayleigh number, which is given by

$$R = \frac{g\beta \frac{dT}{dy} d^4}{\nu \alpha}$$

where $g$ is the acceleration due to gravity and $\beta$ the coefficient of expansion.

In both cases, the onset of convection occurs when a certain critical value of the dimensionless number occurs. A criterion of instability when the coupling, under maximum reinforcement, between the two agencies is taken into account is given by

$$\frac{R}{R_c} + \frac{B}{B_c} \geq 1$$

where $R_c$ and $B_c$ represent the critical values. In general, R and B reinforce each other in such a manner that cellular convection may occur at a Rayleigh number R and a Marangoni number B smaller than their corresponding critical values, $R_c$ and $B_c$.

The similarity between the appearance of Bénard cells and the hexagonal cells attributed to constitutional supercooling (see Fig. 7) is considered in a recent paper (Ref. 10). In this paper certain impurity patterns found in thin alkali halide crystals grown from the melt is attributed to segregation induced by microscale cellular convection.

Mention of various less familiar types of convection is found in the literature. Among these are flows caused by liquid-liquid interfacial tension gradients. Interestingly, a cellular interfacial convection structure was found to accompany the extraction of acetic acid out of ethylene glycol with ethyl acetate (Ref. 11). The suggestion is forwarded that interfacial tension-driven flows may also be important at solid-liquid interfaces (Ref. 12). Thermosolutal convection results in certain situations. In this type of convection the solute concentration varies vertically in a gravity field. The result is a layering of convection regions. The origin for this type of convection lies in the differing rates at which heat and solute diffuse (Ref. 13). Also of pertinence to the present study are the kinds of convective instabilities that occur. These include an oscillatory regime called overstability and a stationary regime called convective instability (Ref. 8b).

## PRESENT INVESTIGATION OF CONVECTION

The present investigation is a natural outgrowth of an investigation of solid-liquid phase change for spacecraft thermal control (Refs. 14 and 15). Both studies contain common problem areas. For example, in both studies a means is needed to predict quantitatively the solidification velocities under zero-g conditions. In the present study, the zero-g condition will be first assumed to be approximated by considering conduction as the only mode of heat transfer. With this assumption, a zone crystal growth of a pure, one-component material is being mathematically modeled. The model being developed will predict melted zone length and solid-liquid interface shapes as a function of rod diameter, material, heater travel rate, and heater power output. The development of a model for a two-component melt will also be undertaken. The models will be experimentally checked with materials whose melts are transparent. The length of the melted zone and interface shapes will thus be readily viewed. The experiments will also investigate the effect of gravity by conducting the zone crystallizations both from the top and from the bottom. That is, the heater will be moved both up and down.

Results of these initial studies are expected to provide a basis for identifying the predominant convective modes as a function of the operating parameters. After this identification is made, the means of describing the convection mathematically will be investigated.

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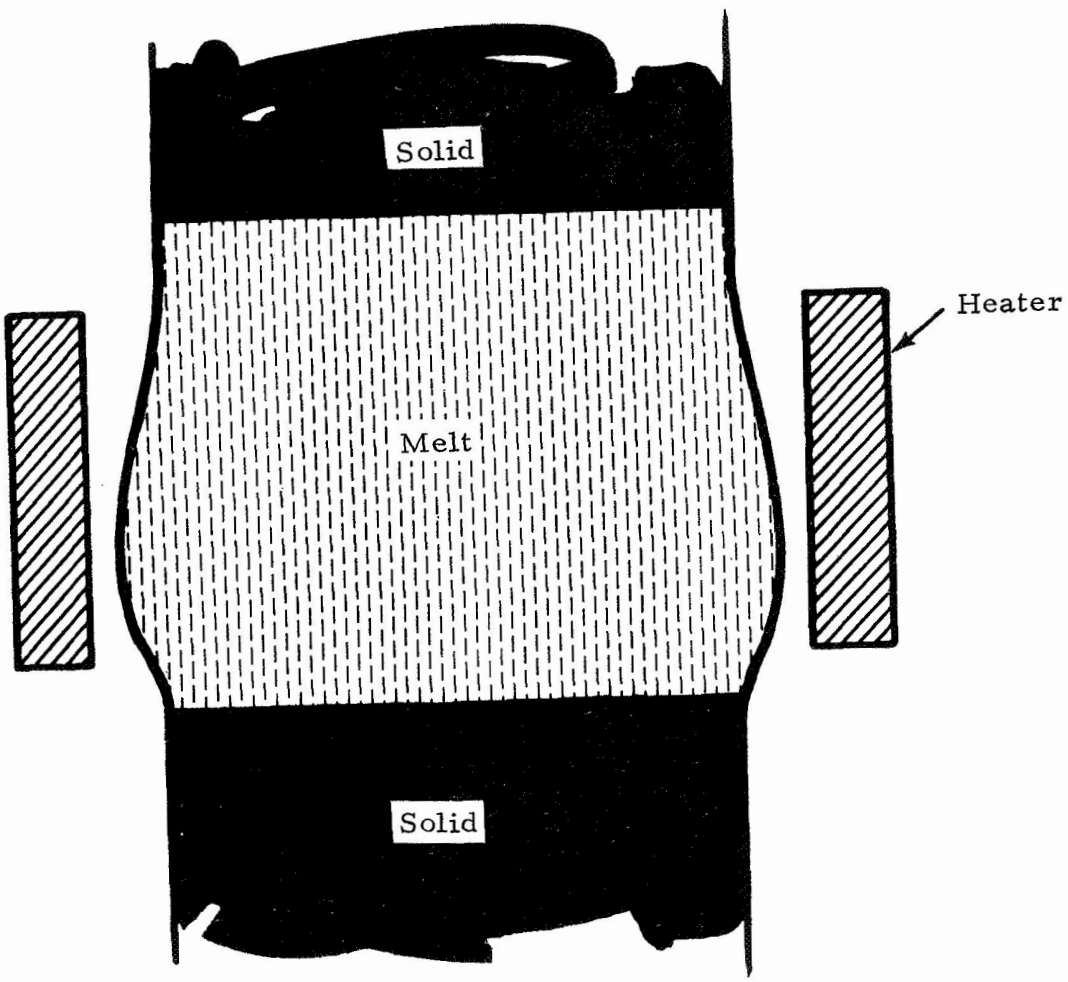


Fig. 1 - Salient Features of a Floating-Zone Crystal Growing Arrangement

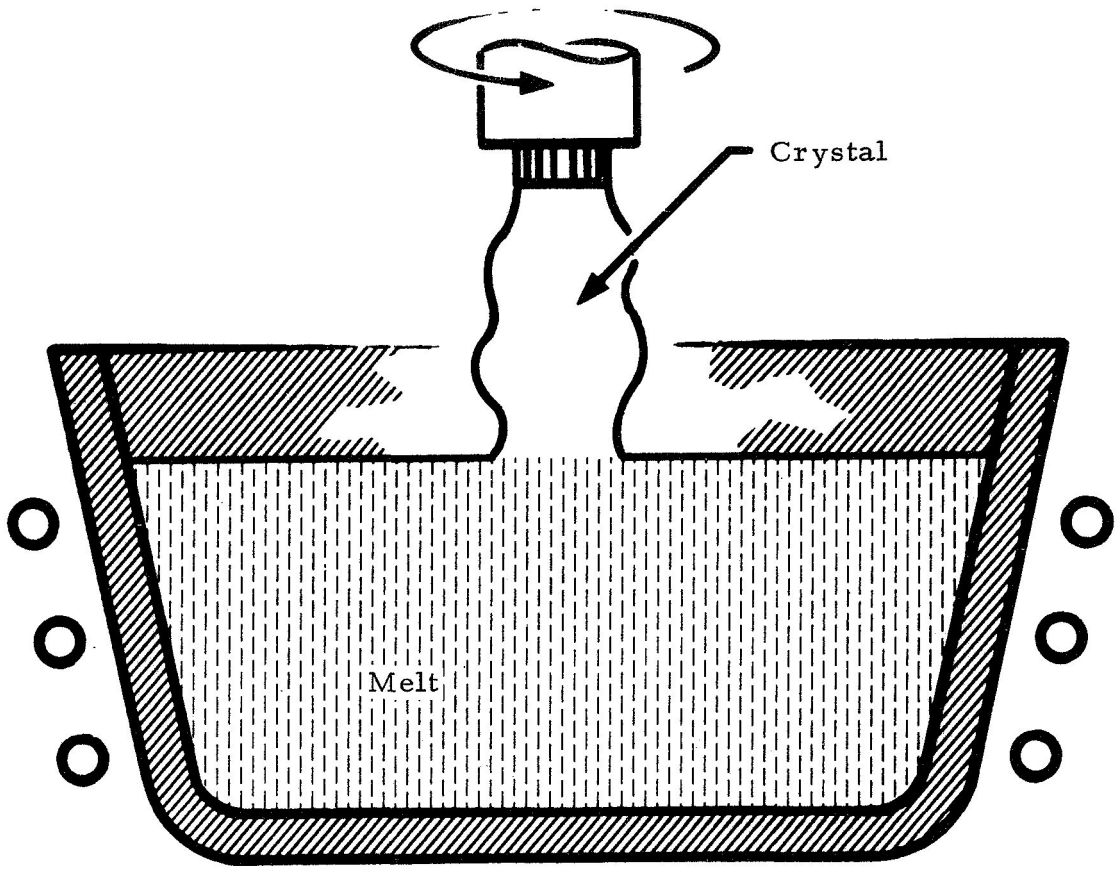


Fig. 2 - Czochralski Crystal-Growing Arrangement

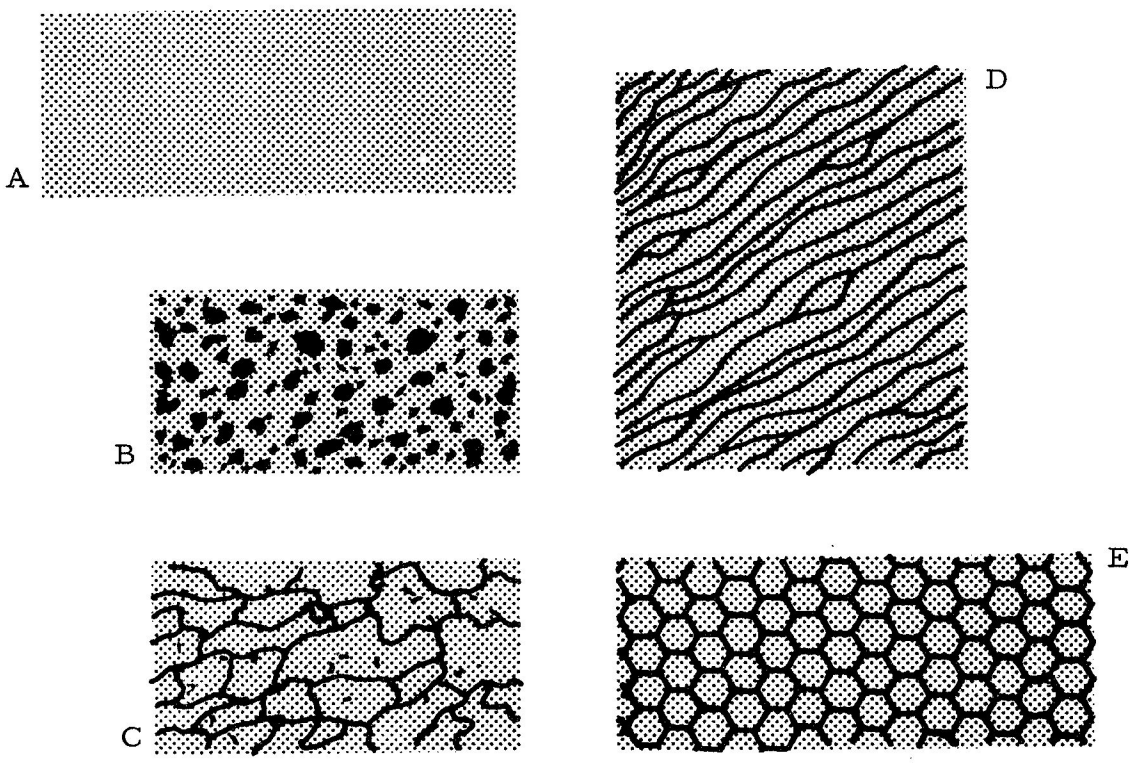


Fig. 3 - Illustration of the Various Morphologies as a Function of Constitutional Supercooling. Supercooling Increases from (A) to (E) (Ref. 3)

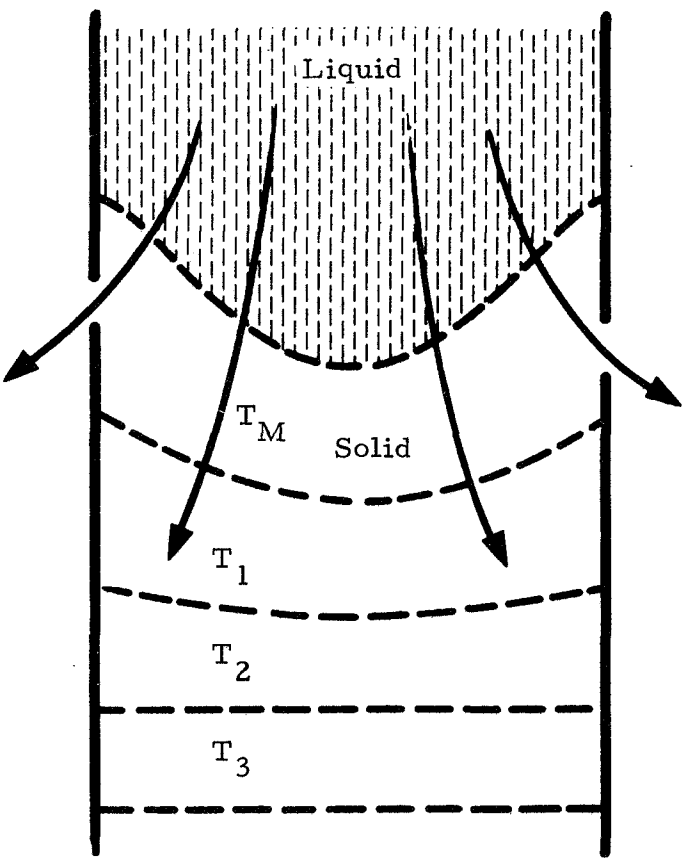


Fig. 4 - Possible Temperature Isotherms in a Crystal During Freezing (Ref. 4)

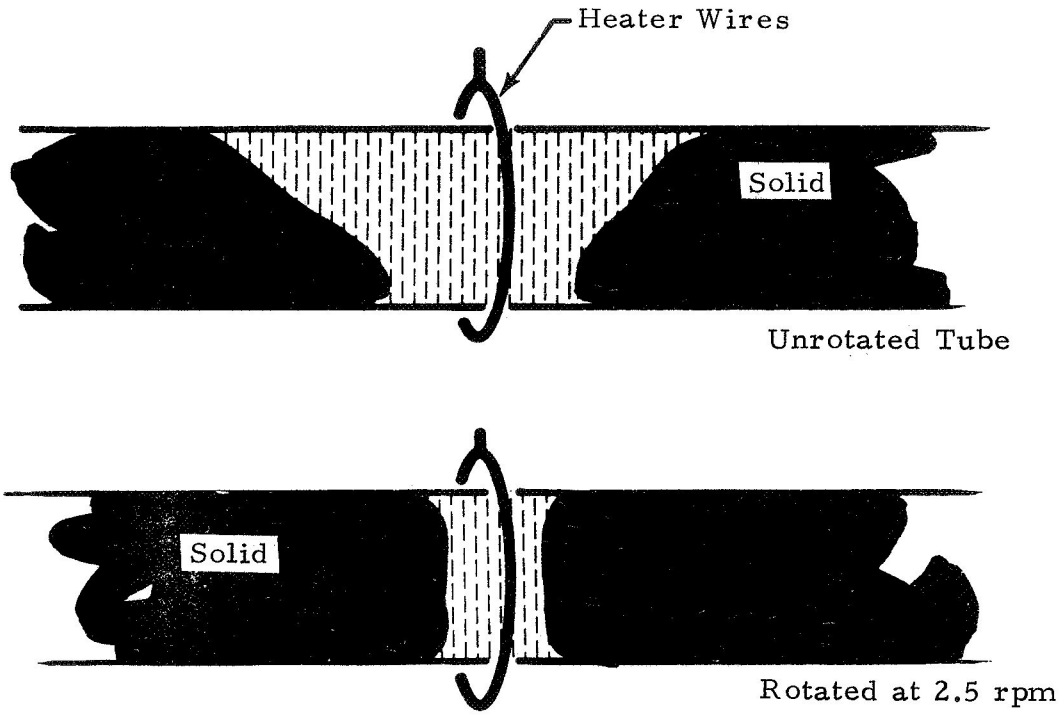


Fig. 5 - Effect of Convection on Solid-Liquid Interface Shapes in Zone-Melting (Ref. 5)

Surface Tension-Driven Cells

Gravity-Driven Cells

Fig. 6 - Fluid Flow Patterns in Bénard and Rayleigh Convection Cells

Hexagonal Cells

Worm-Shape Cells

Fig. 7 - Typical Cell Patterns Caused by Convection (Ref. 10)